

⑫

EUROPEAN PATENT APPLICATION

⑰ Application number 84904169.4

⑮ Int.Cl.⁴: G 11 B 11/10

⑱ Date of filing 15.11.84



⑧⑥ Int. application no: PCT/JP 00547

⑧⑦ Int. publication no: WO 8502292

③⑩ Priority: 17.11.83 JP 216750/83
17.01.84 JP 5634/84
23.03.84 JP 55707/84

④③ Date of publication of application:
08.10.86 Bulletin 86/41

⑧④ Designated Contracting States:
DE FR GB NL

⑦① Applicant: Nippon Sheet Glass Co., Ltd
8 Dosho-machi 4 chome
Higashi-ku Osaka-shi
Osaka 541 (JP)

⑦② Inventor: Gomi Manabu
10-3 Sugano 6-chome, Tchikawa-shi,
Chiba 272 (JP)

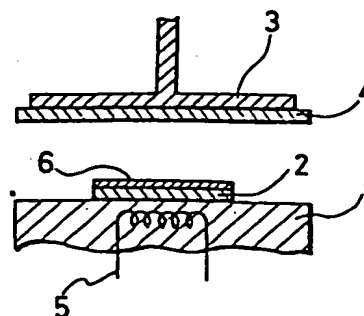
⑦② Inventor: ABE Masanori
6-705, Nishimine-machi 9-chome,
Ota-ku, Tokyo 146 (JP)

⑦④ Representative: Pilch, Adam John Michael
c/o D. Young & Co. 10 Staple Inn
London WC1V 7RD (GB)

⑤④ Method of manufacturing photothermomagnetic recording film.

⑤⑦ A photothermomagnetic recording film manufacturing method in which a perpendicular-magnetization film of a Bi-substituted rare earth iron garnet is formed on a substrate by sputtering a target consisting of an oxide which contains at least Bi atoms, Fe atoms, and rare earth atoms, and then depositing the atoms constituting the oxide which have been released from the target by the sputtering on a substrate which is maintained at a temperature of at most 700°C. Thus it is possible to obtain a perpendicular-magnetization film of Bi-substituted rare earth iron garnet which has a large Bi-substitution quantity (x), and consequently has an extremely large Faraday rotation angle θ_F , a sufficiently large coercive force H_c , as well as a sufficiently small absorption coefficient α . Accordingly it is possible to manufacture a photothermomagnetic recording film which has extremely good photothermomagnetic recording characteristics. Moreover, since it is possible to select the quality of the substrate on which the photothermomagnetic recording film is to be formed, the method is extremely advantageous from the manufacturing point of view.

FIG. 1



S P E C I F I C A T I O N

METHOD OF MANUFACTURING MAGNETO-OPTIC RECORDING FILM

Technical Field

The present invention relates to a method of manufacturing a magneto-optic recording film wherein a Bi-substituted rare-earth iron garnet film with an easy axis of magnetization normal to the film plane is formed on a substrate (hereafter, the vertically magnetized film denotes the film with an easy axis of magnetization normal to the film plane).

Background Art

Iron garnet $R_{3-x}Bi_x(Fe, M)_5O_{12}$ obtained by substituting Bi for R in a rare-earth iron garnet $R_3(Fe, M)_5O_{12}$ is recently receiving much attention as a magneto-optic recording material. Note that in the above formulae, R is a rare-earth element, and M is an atom having a valence of 3 or a group of atoms having a valence equivalent to a valence of 3 such as Al^{3+} , Ga^{3+} , Sc^{3+} , Tl^{3+} , $(Co^{2+} + Ti^{4+})$ or the like. In the Bi-substituted rare-earth iron garnet, since some Rs are substituted with Bi, the Faraday rotation angle θ_F can be increased without much increasing the absorption coefficient α and, therefore, this material is generally an excellent magneto-optic recording material.

In order to improve performance of a magneto-optic material of the Bi-substituted rare-earth iron garnet having such a property, the Bi substitution amount x must be increased, which results in the increase of the Faraday rotation angle θ_F . Conventionally, in a sintered ceramics of a rare-earth iron garnet, the Bi solid solution limit is known to be 50% of the

dodecahedral site of the crystal structure. So monocrystalline films having a large Bi substitution amount x have been studied intensively.

A highly Bi-substituted rare-earth iron garnet thin film as described above is normally manufactured by the liquid phase epitaxy (LPE) method as described, e.g., in J.J. A. P., 19, 2105 (1980). However, a magnetic thin film manufactured by the liquid phase epitaxy method, wherein the film composition is $\text{Bi}_{0.6}\text{Sm}_{1.2}\text{Er}_{1.2}\text{Ga}_{1.0}\text{Fe}_{4.0}\text{O}_{12}$ has a small Faraday rotation angle θ_F of about 2.4 degree/ μm at a light wavelength $\lambda = 500 \text{ nm}$ at which the Faraday rotation angle is expected to be maximum value. Such a small Faraday rotation angle is impractical.

Further, in LPE method, a Bi-substituted rare-earth iron garnet film must be formed on a single crystal substrate such as gadolinium gallium garnet $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (to be referred to as a GGG substrate hereafter) which is high is cost. However, a method capable of forming a highly Bi-substituted rare-earth iron garnet thin film on an amorphous substrate such as a glass substrate which has a high productivity has been desired. Although various studies have been made to provide such a method, a Bi-substituted rare-earth iron garnet thin film formed on an amorphous substrate obtained so far has been a polycrystalline film having a magnetization parallel to the film plane. A vertically magnetized film desired as a magneto-optic recording material has not yet been obtained.

Disclosure of Invention

An object of the present invention is to provide a method of manufacturing a magneto-optic recording film which is free from the above-mentioned drawbacks of the conventional methods.

In the conventional LPE method, a thin film must be grown at a high temperature of about 800°C. However, since the vapor pressure of Bi is extremely high, i.e., about 1 Torr, Bi is selectively vaporized from the melt during thin film formation by the LPE method. In view of this problem, the present invention is based on the concept that the LPE method is not suitable for forming a thin film of a Bi-substituted rare-earth iron garnet containing a high concentration of Bi. According to the estimation made by the present inventors, the Bi substitution amount x in a monocrystalline thin film which has been formed so far by conventional LPE methods using a GGG substrate is at best about 20% of the dodecahedral site of the rare-earth iron garnet.

In a method of manufacturing a magneto-optic recording film wherein a vertically magnetized film of a Bi-substituted rare-earth iron garnet is formed on a substrate, a method in the present invention is characterized in that a target consisting of an oxide containing at least Bi atoms, Fe atoms and rare-earth element atoms is sputtered, and the atoms constituting the oxide which are released from the target by sputtering are deposited on the substrate held at a temperature of 700°C or lower, thereby forming the vertically magnetized film of the Bi-substituted rare-earth iron garnet. With this method, a vertically magnetized film of a Bi-substituted rare-earth iron garnet having a large Bi substitution amount x , a very large Faraday rotation angle θ_F , a sufficiently large coercive force H_C and a sufficiently small absorption coefficient α can be manufactured, so that a film having excellent magneto-optic recording characteristics can be manufactured. In addition, since the material of the substrate on which a magneto-optic recording film is formed can be selected from various materials, the

method is extremely advantageous from the manufacturing point of view.

Examples of the target consisting of an oxide containing at least Bi atoms, Fe atoms and rare-earth element atoms include targets having a general formula $(\text{Bi}_2\text{O}_3)_x(\text{R}_2\text{O}_3)_y(\text{Fe}_2\text{O}_3)_z(\text{M}_2\text{O}_3)_u$ wherein $0 < x \leq 3/2$, $0 < y \leq 3/2$, $0 < z \leq 5/2$, and $0 \leq u \leq 5/2$, R is a rare-earth element such as Y or Sm, and M is Al^{3+} , Ga^{3+} , Sc^{3+} , Tl^{3+} , $(\text{Co}^{2+} + \text{Ti}^{4+})$ or the like.

Of such targets, a target wherein $0 < y \leq 3/2$, $1 < (2/3)x + y \leq 3/2$, $3/2 < z \leq 5/2$, and $z + u = 5/2$ is preferable.

Although a sintered ceramics which is easy to handle is preferable as the target, the target is not limited to a sintered ceramics. A mixture containing elements of the above formula can be used instead.

In order to form a thin film of a Bi-substituted rare-earth iron garnet having a single phase garnet structure by the above-mentioned sputtering method, the thin film composition must have a general formula $\text{Bi}_a\text{R}_b(\text{Fe}, \text{M})_5\text{O}_{12}$ ($0 < a \leq 3$, $2 < a + b \leq 3$). If $a + b$ is 2 or less, too many defects are formed and a single phase garnet structure cannot be obtained. On the other hand a thin film formed by the sputtering method has a Bi content lower than that of the target due to scattering of Bi during sputtering. Under the sputtering conditions performed by the present inventors, the amount of Bi in the formed film is estimated to be about 2/3 of that in the target.

Since a thin film containing a large amount of Bi can be formed by using a target containing a larger amount of Bi, in order to form a thin film containing a larger amount of Bi than a solid solution limit so far reported, a target containing a large amount of Bi,

e.g., $\text{Bi}_a\text{R}_b(\text{Fe}, \text{M})_5\text{O}_{12}$ ($1.5 < a \leq 9/2$, $2 < (2/3)a + b \leq 3$) is preferably used. When a target having the above composition is formed into a polycrystalline sintered ceramics, it will not consist of a single phase garnet structure but will be mixture consisting of both the garnet phase and other impurity phases. However, such a target is preferably used since it has a high Bi content. In particular, the Bi substitution amount x is preferably 2 or more.

According to a method of manufacturing a magneto-optic recording film of the present invention, the target is sputtered and the atoms constituting the target are deposited on a substrate which is kept at a temperature of 700°C or lower. When the substrate is kept at a temperature higher than 700°C , the vapor pressure of Bi is too high that a thin film having a large Bi substitution amount x as an objective of the present invention cannot be obtained.

Describing the method of manufacturing a magneto-optic recording film according to the present invention in more detail, the method is classified into the following two cases depending upon the material of a substrate used for forming a magneto-optic recording film and the properties of the thin film. In the first case, a (111) oriented GGG substrate is used as a substrate and a monocrystalline thin film of a Bi-substituted rare-earth iron garnet is formed on this substrate. In the second case, any substrate including an amorphous substrate such as glass or the like is used, and a vertically magnetized film of a Bi-substituted rare-earth iron garnet is formed on the substrate.

When a monocrystalline thin film is formed on a GGG substrate, the substrate must be kept at a temperature of 350 to 700°C . When the substrate

temperature is lower than 350°C, the thin film formed will be amorphous and a monocrystalline thin film cannot be obtained. When a target represented by $\text{Bi}_a\text{R}_b(\text{Fe}, \text{M})_5\text{O}_{12}$ ($0 < a \leq 9/2$, $2 < (2/3)a + b \leq 3$) or the like is sputtered, a monocrystalline thin film of a Bi-substituted rare-earth iron garnet can be formed. In order to obtain better magnetic characteristics of the monocrystalline thin film, a heat-treatment such as re-heating or gradual cooling can be performed.

When any substrate including an amorphous substrate such as glass or metal, semiconductor, insulator is used, the vertically magnetized film of the polycrystalline Bi-substituted rare-earth iron garnet is obtained through crystallization by annealing of the amorphous film deposited on the substrate kept at 500°C or lower. Herein, the amorphous film must have a composition corresponding to that of a Bi-substituted rare-earth iron garnet.

When sputtering on any substrate other than the above monocrystalline substrate (e.g., glass substrate) is performed at a substrate temperature higher than 500°C, an amorphous thin film cannot be obtained, and a crystalline magnetic thin film having a roughened surface is directly formed. However, when an amorphous thin film is formed and is then annealed to crystallize the film, a polycrystalline vertically magnetized film of a Bi-substituted rare-earth iron garnet film with magnetic anisotropy perpendicular to the film plane which has less surface roughness can be formed.

Describing in more detail, the method of manufacturing a polycrystalline vertically magnetized film of a Bi-substituted rare-earth iron garnet film with magnetic anisotropy perpendicular to the film plane includes the following two cases; the case of forming

a protective film after forming the amorphous thin film and the case of not forming such a protective film.

When annealing is performed without forming a protective film on the amorphous thin film, the substrate temperature during formation of the amorphous thin film is preferably kept at 300 to 500°C and more preferably at 400 to 450°C. An amorphous thin film formed at a substrate temperature lower than 300°C tends to result in a magnetic thin film which develops surface roughness upon annealing and is not preferable.

When a protective film is formed on the amorphous thin film as described above, surface roughness upon crystallization by annealing and vaporization of Bi are prevented, and a vertically magnetized film having a smoother surface can be formed.

The substrate temperature must be 500°C or lower for the reasons described above. The protective film can be selected from various films which do not react with a formed thin film at an annealing temperature of, e.g., about 700°C. Examples of such films may include oxide films such as SiO_2 , ZnO , TiO_2 or CeO_2 , nitride films such as Si_3N_4 , and fluoride films such as BaF_2 or CaF_2 . The thickness of the protective film must be 500 Å or more.

Annealing for crystallizing the amorphous thin film is preferably performed at a temperature of 500 to 900°C. When the annealing temperature is lower than 500°C, crystallization cannot be easily started, which is not desirable. However, when the annealing temperature is higher than 900°C, vaporization of Bi may occur and a reaction between the substrate and the thin film may occur, which is not desirable.

Brief Description of Drawings

Fig. 1 is a sectional view showing a first embodiment of the present invention together with an RF sputtering apparatus used in this embodiment.

Figs. 2 and 3 are graphs showing the substrate temperature dependence of the Faraday rotation angle θ_F and the coercive force H_C , respectively, of $(Y, Bi)_3(Fe, Al)_5O_{12}$ monocrystalline thin film manufactured by the first embodiment of the present invention.

Figs. 4 and 5 are graphs showing the light wavelength dependence of the Faraday rotation angle θ_F for samples 5 and 3 shown in Figs. 2 and 3, respectively.

Fig. 6 is a graph showing the light wavelength dependence of an absorption coefficient α for sample 5 shown in Figs. 2 and 3.

Fig. 7 is a graph showing the temperature dependence of the Faraday rotation angle θ_F for sample 5 shown in Figs. 2 and 3.

Fig. 8 is a graph showing the hysteresis characteristics for sample 4 shown in Figs. 2 and 3.

Figs. 9 to 11 are graphs showing the hysteresis characteristics for sample 5 shown in Figs. 2 and 3 for three different thicknesses thereof.

Fig. 12 is a sectional view showing a second embodiment according to the present invention together with an RF sputtering apparatus used in this embodiment.

Fig. 13 is a graph showing the hysteresis characteristics of a $(Y, Bi)_3(Fe, Al)_5O_{12}$ thin film manufactured by the second embodiment of the present invention.

Fig. 14 is a sectional view showing a third embodiment of the present invention together with an RF sputtering apparatus used in this embodiment.

Best Mode of Carrying Out the Invention

A method of manufacturing a magneto-optic recording film according to the present invention will be described with reference to embodiments applied to the manufacture of a thin film of a Bi-substituted rare-earth iron garnet represented by $(Y, Bi)_3(Fe, Al)_5O_{12}$, referring to the accompanying drawings.

$(Y, Bi)_3(Fe, Al)_5O_{12}$ is obtained by partially substituting Y in a yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG) with Bi and partially substituting Fe thereof with Al. When Y is partially substituted with Bi, the Faraday rotation angle θ_F can be increased without much increasing the absorption coefficient α . When Fe is partially substituted with Al, the absorption coefficient α and Curie temperature can be decreased, and the saturation magnetization can be reduced to allow easy manufacture of a vertically magnetized film.

The first embodiment of the present invention will now be described with reference to Fig. 1.

Referring to Fig. 1, a (111) oriented monocrystalline GGG substrate 2 is placed on a stainless steel electrode plate 1 also serving as a sample table of an RF sputtering apparatus. A target 4 is mounted on an electrode plate 3. The target 4 is a sintered ceramics disk of a polycrystalline iron garnet (a composition: $Bi_{2.0}Y_{1.0}Fe_{3.8}Al_{1.2}O_{12}$) with other impurity phases. Since a heater 5 is mounted on the electrode plate 1, the GGG substrate 2 is heated to a predetermined temperature by the heater 5 through the electrode plate 1.

After the interior of the sputtering apparatus is evacuated to a predetermined degree of vacuum, a mixture gas of Ar and O_2 (Ar : O_2 = 9 : 1) is supplied into the sputtering apparatus to a pressure of about 7 Pa. When the degree of vacuum is stabilized, a predetermined RF

voltage is applied between the electrode plates 1 and 3 so as to start glow discharge. Ar^+ ions generated by discharge sputter the surface of the target 4, and this sputtering releases atoms such as Bi, Y, Fe, Al and O from the target 4. The released atoms are deposited on the GGG substrate 2 which is heated to the predetermined temperature, and a monocrystalline thin film 6 of $(\text{Y}, \text{Bi})_3(\text{Fe}, \text{Al})_5\text{O}_{12}$ is epitaxially grown on the GGG substrate 2. When the sputtering power was 110 W and the sputtering time was 5 hours, the obtained thin film 6 had a thickness of $1.5 \mu\text{m}$.

The thin film 6 is annealed together with the GGG substrate 2 having the film 6 thereon under predetermined conditions so as to remove strain in the thin film 6. X-ray diffractometry of the thin film 6 thus obtained revealed that the film 6 was monocrystalline.

When the monocrystalline thin film 6 manufactured in the first embodiment was observed through an optical microscope, it had an arabesque magnetic domain structure and was proved to be an excellent magnetic thin film having superior characteristics as shown in Figs. 2 to 11. The measurement results will sequentially be described hereinbelow. When the Faraday rotation angle θ_F shown in Figs. 2 and 7 to 11 was measured, a He-Ne laser (wavelength: 6328 \AA) was used as a light source. Measurement was performed by transmitting light through the thin film 6.

✓ Measurement of the Curie point shown in Fig. 7 was performed for a sample having a three-layered structure consisting of a GGG substrate 2 having an Al film as a reflecting film on a thin film 6. ✓

Figs. 2 and 3 are graphs showing the Faraday rotation angle θ_F and the coercive force H_C of thin

films 6 (respective samples are represented by reference numerals 1 to 6, respectively) manufactured at respective substrate temperatures of 420°C, 470°C, 490°C, 510°C, 550°C and 620°C. As shown in Fig. 2, the thin films 6 manufactured on the GGG substrate 2 at 420 to 620°C had Faraday rotation angles θ_F of 1 to 2.75 degree after annealing. Annealing was performed in air at 640°C for 5 hours for samples 1 and 2 and at 740°C for 5 hours for samples 3 to 6. The Faraday rotation angles θ_F of the thin films 6 manufactured in this embodiment are considerably larger than that of a Bi-substituted rare-earth iron garnet thin film manufactured by the above-mentioned LPE method, i.e., about 0.5 degree.

Measurement of the crystal lattice constant of the thin films 6 by X-rays revealed that the thin films 6 of the embodiment had a Bi content up to a solid solution limit (50% of the dodecahedral site). Therefore, it was found that a large Faraday rotation angle θ_F was obtained by substitution with a large amount of Bi.

The thin films 6 according to the embodiment of the present invention had coercive forces H_C as high as 140 to 350 Oe, as shown in Fig. 3.

Figs. 2 and 3 show the Faraday rotation angle θ_F and the coercive force H_C of each as-sputtered film 6 together with the data of the Faraday rotation angle θ_F and the coercive force H_C of the film 6 after annealing. Among the samples shown in Figs. 2 and 3, sample 6 (substrate temperature: 620°C) had a film thickness of 2.0 μm (sputtering time: 7 hours), and remaining five samples (substrate temperatures: 420 to 550°C) had a thickness of 1.5 μm .

Fig. 4 shows the light wavelength dependence of the Faraday rotation angle θ_F of sample 5 (substrate temperature: 550°C), and Fig. 5 shows the light

wavelength dependence of the Faraday rotation angle θ_F of sample 3 (substrate temperature: 490°C). As can be seen from these graphs, the Faraday rotation angle θ_F in the range of $\lambda = 0.4$ to $0.7 \mu\text{m}$ is 1 to 10 degree for sample 5 and 1 to 20 degree for sample 3 after annealing; these values are very large. For both the samples, it can be seen that the Faraday rotation angle θ_F is very large near a wavelength of $0.5 \mu\text{m}$. Fig. 4 also shows the measurement result of the as-sputtered film 6 for comparison.

Fig. 6 shows the wavelength dependence of the absorption coefficient α of the thin film 6 (sample 5). It can be seen from Fig. 6 that the absorption coefficient α of sample 5 is sufficiently small for visible light having a wavelength of $0.55 \mu\text{m}$ or more; the thin film 6 is substantially transparent to light in this wavelength range and has an absorption edge near $0.5 \mu\text{m}$.

Fig. 7 shows temperature dependence of the Faraday rotation angle θ_F for sample 5. It is seen from Fig. 7 that the Faraday rotation angle θ_F of sample 5 monotonously decreases with an increase in temperature T from room temperature to about 170°C. Fig. 7 also indicates that the Curie temperature T_C is 164°C. The slow change in the Faraday rotation angle θ_F at temperature $T = 160$ to 200°C may be attributed to the residual strain and random arrangement of Fe and Al atoms in the thin film 6.

Fig. 8 shows the hysteresis characteristics of the Faraday rotation angle θ_F of sample 4 (substrate temperature: 510°C) as a function of a magnetic field H applied along a direction perpendicular to the film plane. As can be seen from this figure, the hysteresis characteristics change before and after annealing and the Faraday rotation angle θ_F increases after annealing.

Figs. 9 to 11 show the hysteresis characteristics

of the thin film 6 of sample 5 after annealing, for three different film thicknesses, at the central portion (film thickness: $1.5 \mu\text{m}$) and this peripheral portions (film thicknesses: $1.2 \mu\text{m}$ and $0.9 \mu\text{m}$), i.e., 1.5 , 1.2 and $0.9 \mu\text{m}$. It can be seen from these figures that the smaller the film thickness, the better the squareness of the loop, and especially when the film thickness is $1 \mu\text{m}$ or less, the film exhibits particularly preferable hysteresis characteristics for magneto-optic recording applications.

As can be seen from the above results, the $(\text{F}, \text{Bi})_3(\text{Fe}, \text{Al})_5\text{O}_{12}$ monocrystalline thin film 6 manufactured in the first embodiment has a very large Faraday rotation angle θ_F , a sufficiently large coercive force H_c and a very small absorption coefficient α , thereby providing highly desirable properties as a magneto-optic recording material.

The second embodiment of the present invention will now be described with reference to Fig. 12.

First, as shown in Fig. 12, an amorphous quartz glass is used as the substrate 7, and is heated to 440°C . A target 4 similar to that of the first embodiment is used, and the target 4 is sputtered under similar conditions to those in the first embodiment, thereby forming $(\text{Y}, \text{Bi})_3(\text{Fe}, \text{Al})_5\text{O}_{12}$ thin film 6 on the quartz glass substrate 7. When the sputtering power was 110 W and the sputtering time was 2 hours and a half, the obtained thin film 6 had a thickness of $0.8 \mu\text{m}$.

The thin film 6 obtained in this manner was annealed in air at 700°C for 3 hours so as to crystallize the thin film 6.

When crystal structure of the thin film 6 manufactured in the second embodiment was examined by X-ray diffractometry, the film was proved to be a

polycrystalline film having no preferred orientation. An optical microscope measurement showed that although the film is polycrystalline, it has an arabesque bubble-like magnetic domain structure and was an excellent vertically magnetized film having the following superior characteristics.

More specifically, as shown in Fig. 13, the hysteresis of the Faraday rotation angle θ_F of the thin film 6 as a function of a magnetic field H applied along a direction perpendicular to the film plane exhibited an excellent squareness. The magnetic torque measurement revealed that the film is a vertically magnetized film. The film had a large Faraday rotation angle θ_F of about 1.5 degree and a sufficiently large coercive force H_C of about 200 Oe. Thus, the thin film 6 has very desirable properties as a magneto-optic recording material. These may indicate that the film 6 contains the large amount of Bi up to its solid solution limit, applying a large perpendicular magnetic anisotropy. In Fig. 13, a light source for measuring the Faraday rotation angle θ_F was a He-Ne laser (wavelength: 6328 Å). The measurement was performed by transmitting light through the thin film 6.

The thin film 6 formed in this manner has relatively small surface roughness adequate to the magneto-optic recording applications.

In this manner, according to the second embodiment, a highly Bi-substituted rare-earth iron garnet thin film which has excellent vertical magnetization characteristics although it is polycrystalline can be formed on a quartz glass substrate having a good productivity.

The magnetic thin film manufactured in the second embodiment allows direct formation of a reflecting

layer thereon, and therefore can be magneto-optic recording medium able to thermomagnetically write using a light with a relatively low power.

The third embodiment of the present invention will now be described with reference to Figs. 12 and 14.

By a sputtering method similar to that in the second embodiment, an amorphous thin film 6 of $(Y, Bi)_3(Fe, Al)_5P_{12}$ having a film thickness of $0.8 \mu m$ is formed on a quartz glass substrate 7 heated to $440^\circ C$, as shown in Fig. 12.

Then, as shown in Fig. 14, after replacing a target 4 mounted on an electrode plate 1 with a target 8 of SiO_2 , similar sputtering is performed using the target 8, thereby forming an SiO_2 layer 9 on the thin film 6. During this film formation, the quartz glass substrate 7 is held at room temperature. When the sputtering power was 200 W and the sputting time was 30 minutes, the obtained SiO_2 layer 9 had a thickness of $0.5 \mu m$.

A sample having a three-layered structure consisting of the quartz glass substrate 7, the thin film 6 and the SiO_2 layer 9 was annealed in air at $700^\circ C$ for 3 hours.

When X-ray diffractometry was performed, the thin film 6 manufactured in this manner had no preferred orientation as in the case of the thin film 6 manufactured in the second embodiment. When the film 6 was observed through an optical microscope, although it was polycrystalline it was found to have an arabesque bubble-like magnetic domain structure and to be an excellent vertically magnetized film having excellent characteristics equivalent to those shown in Fig. 13. In this embodiment, due to the presence of the protective film constituted by the SiO_2 layer 9,

out-diffusion of atoms such as Bi contained in the thin film 6 and surface roughening during annealing can be prevented, and growth of crystal grains of the thin film 6 can be suppressed.

In this manner, according to the third embodiment of the present invention, as in the case of the second embodiment, a polycrystalline vertically magnetized film having excellent characteristics can be formed on a quartz glass substrate 7 having an excellent productivity. In addition, due to the presence of an SiO_2 layer 9 as a protective film, surface roughness of the thin film 6 resulting from annealing to crystallize the film can be more effectively prevented than in the second embodiment. Since out-diffusion of Bi from the thin film 6 during annealing can be prevented by the SiO_2 layer 9, the annealing temperature can be set to be higher than that in the second embodiment.

C L A I M S

1. A method of manufacturing a magneto-optic recording film wherein a vertically magnetized film of a Bi-substituted rare-earth iron garnet is formed on a substrate, characterized in that a target consisting of an oxide containing at least Bi atoms, Fe atoms and rare-earth element atoms is sputtered, and the atoms constituting the oxide which are released from the target by sputtering are deposited on the substrate which is held at a temperature of 700°C or lower, thereby forming the vertically magnetized film consisting of the Bi-substituted rare-earth iron garnet.

2. A method according to claim 1, wherein the target has a formula $(\text{Bi}_2\text{O}_3)_x(\text{R}_2\text{O}_3)_y(\text{Fe}_2\text{O}_3)_z(\text{M}_2\text{O}_3)_u$ {wherein R is a rare-earth element, M is an atom having a valence of 3 or a group of atoms having a valence equivalent to a valence of 3, and $0 < x \leq 3/2$, $0 < y \leq 3/2$, $0 < z < 5/2$, and $0 \leq u \leq 5/2$ }.

3. A method according to claim 1, wherein the target has a formula $(\text{Bi}_2\text{O}_3)_x(\text{R}_2\text{O}_3)_y(\text{Fe}_2\text{O}_3)_z(\text{M}_2\text{O}_3)_u$ {wherein R is a rare-earth element, M is an atom having a valence of 3 or a group of atoms having a valence equivalent to a valence of 3, and $0 < y \leq 3/2$, $1 < (2/3)x + y \leq 3/2$, $3/2 < z \leq 5/2$, and $z + u = 5/2$ }.

4. A method according to claim 1, wherein the target is a sintered ceramics consisting of coexisting multiple phases having a formula $\text{Bi}_a\text{R}_b(\text{Fe}, \text{M})_5\text{O}_{12}$ {wherein R is a rare-earth element, M is an atom having a valence of 3 or a group of atoms having a valence

equivalent to a valence of 3, and $1.5 < a \leq 9/2$ and $2 < (2/3) a + b \leq 3$ }.

5. A method according to any one of claims 2 to 4, wherein the atom having a valence of 3 or the group of atoms having a valence equivalent to a valence of 3 represented by M is selected from the group consisting of Al^{3+} , Ga^{3+} , Sc^{3+} , Ti^{3+} , and $(\text{Co}^{2+} + \text{Ti}^{4+})$.

6. A method according to any one of claims 1 to 5, wherein the substrate is a (111) oriented monocrystalline gadolinium gallium garnet substrate.

7. A method according to claim 6, wherein the substrate temperature is 350 to 700°C.

8. A method according to claim 1, wherein an amorphous thin film which can be converted into a Bi-substituted rare-earth iron garnet by iron garnet by crystallization is formed by sputtering, and the amorphous thin film is crystallized by annealing.

9. A method according to claim 8, wherein the substrate is a glass substrate.

10. A method according to claim 8, wherein the substrate temperature is 300 to 500°C.

11. A method according to claim 8, wherein the substrate temperature is 400 to 450°C.

12. A method according to claim 8, wherein the annealing temperature is 500 to 900°C.

13. A method according to claim 8, wherein an amorphous thin film which can be converted into a Bi-substituted rare-earth iron garnet by crystallization is formed on the substrate by sputtering, a protective film for preventing vaporization of Bi is formed on the amorphous thin film, and annealing is performed so as to crystallize the amorphous Bi-substituted rare-earth iron garnet.

14. A method according to claim 13, wherein the protective film is one member selected from the group consisting of an SiO_2 film, a ZnO film, a TiO_2 film, a CeO_2 film, a Si_3N_4 film, a BaF_2 film and a CaF_2 film.

15. A method according to claim 13, wherein the protective film has a thickness of 500 Å or more.

FIG. 1

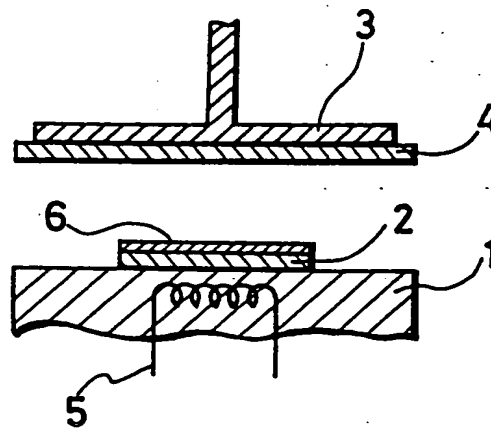
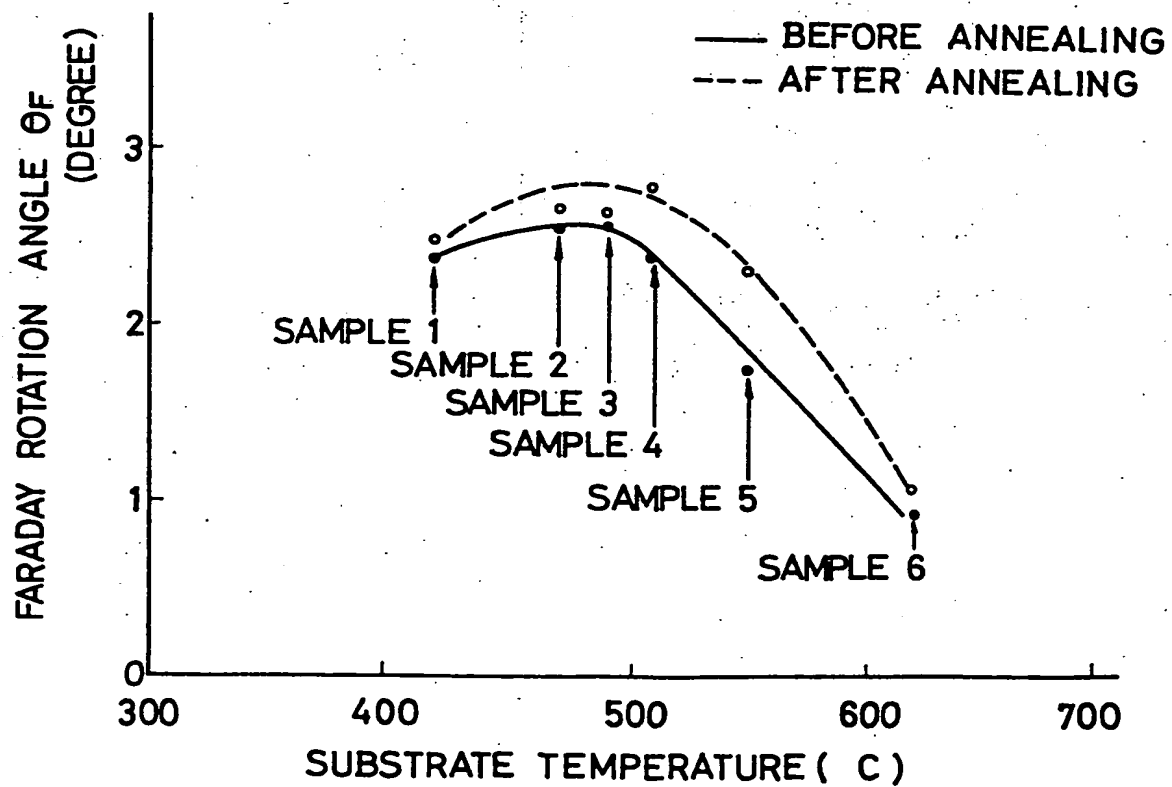


FIG. 2



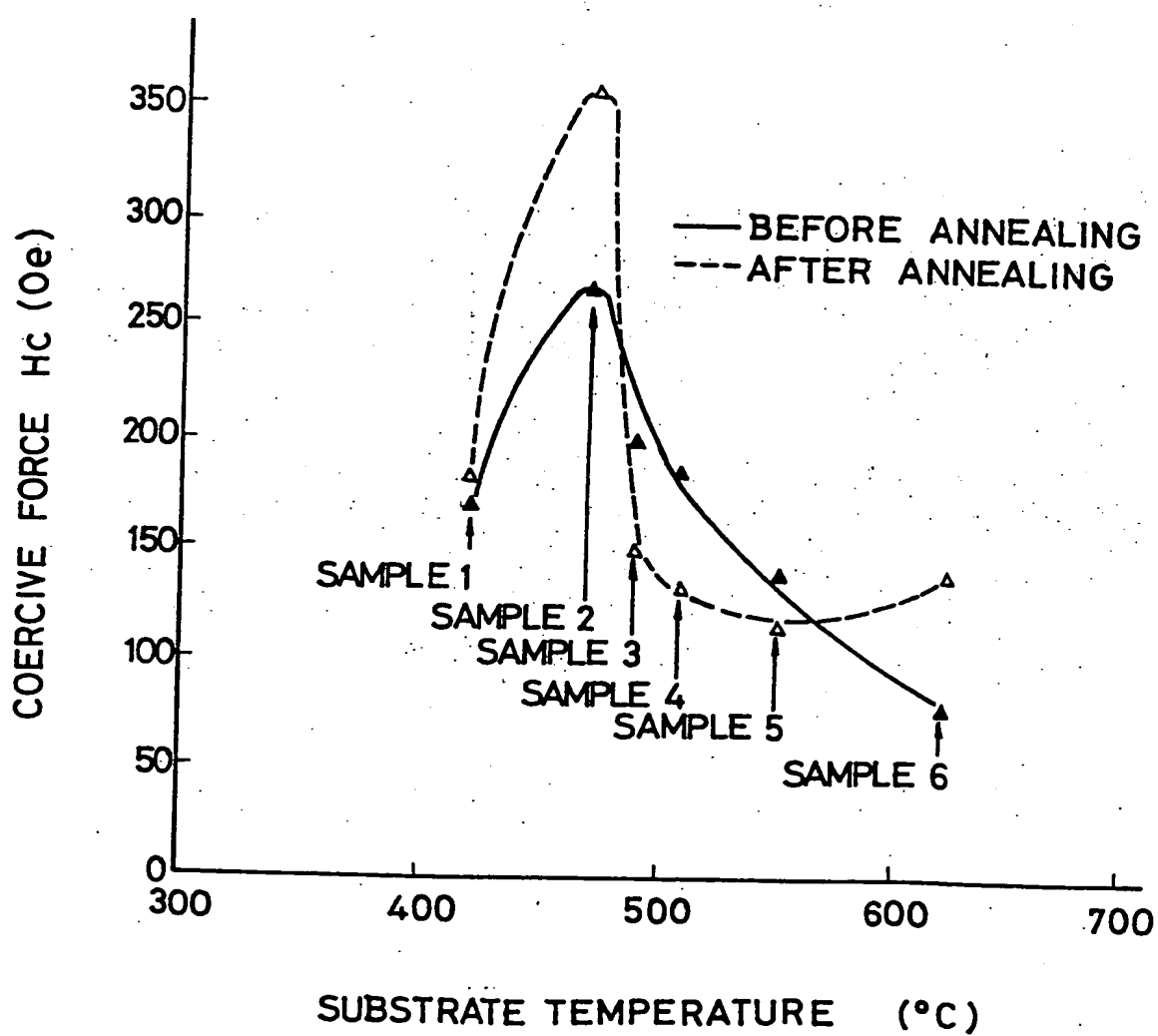
2/7
FIG. 3

FIG. 4

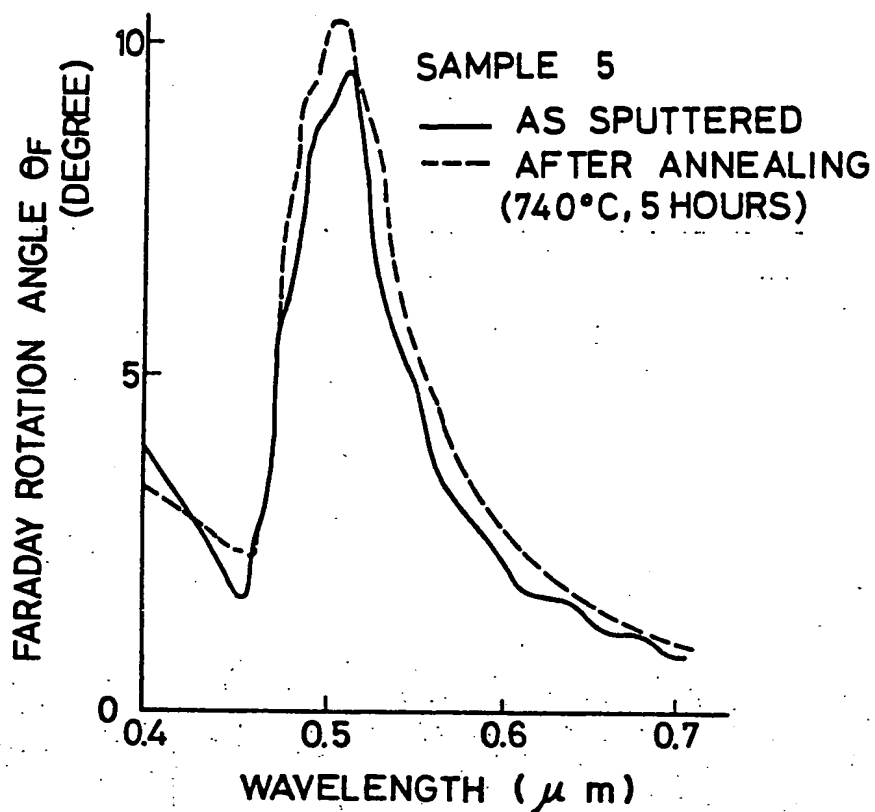
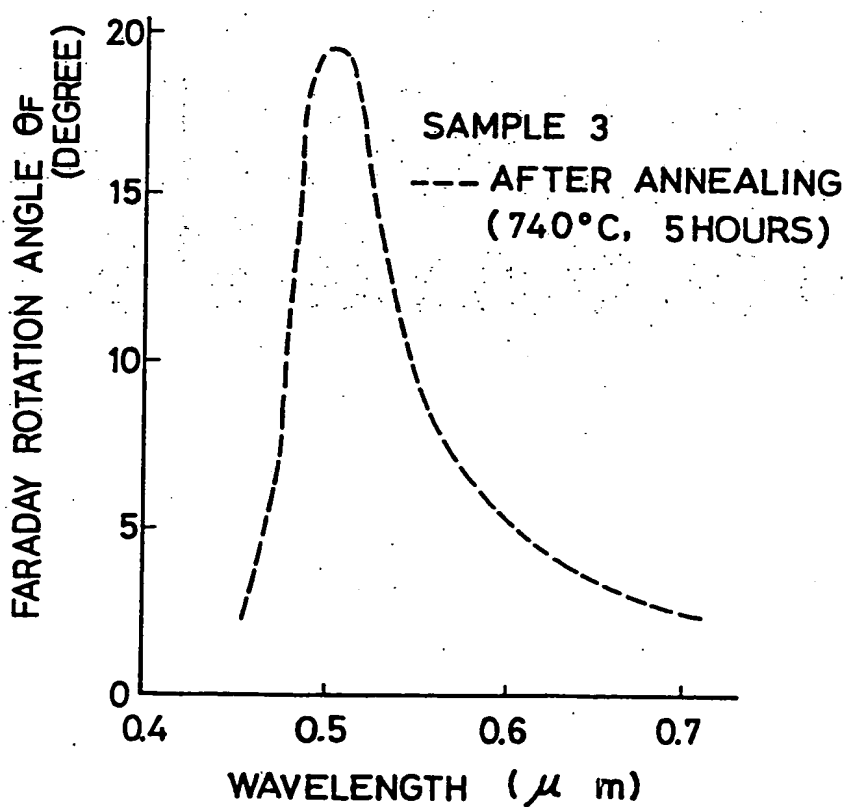
 $\frac{3}{7}$ 

FIG. 5



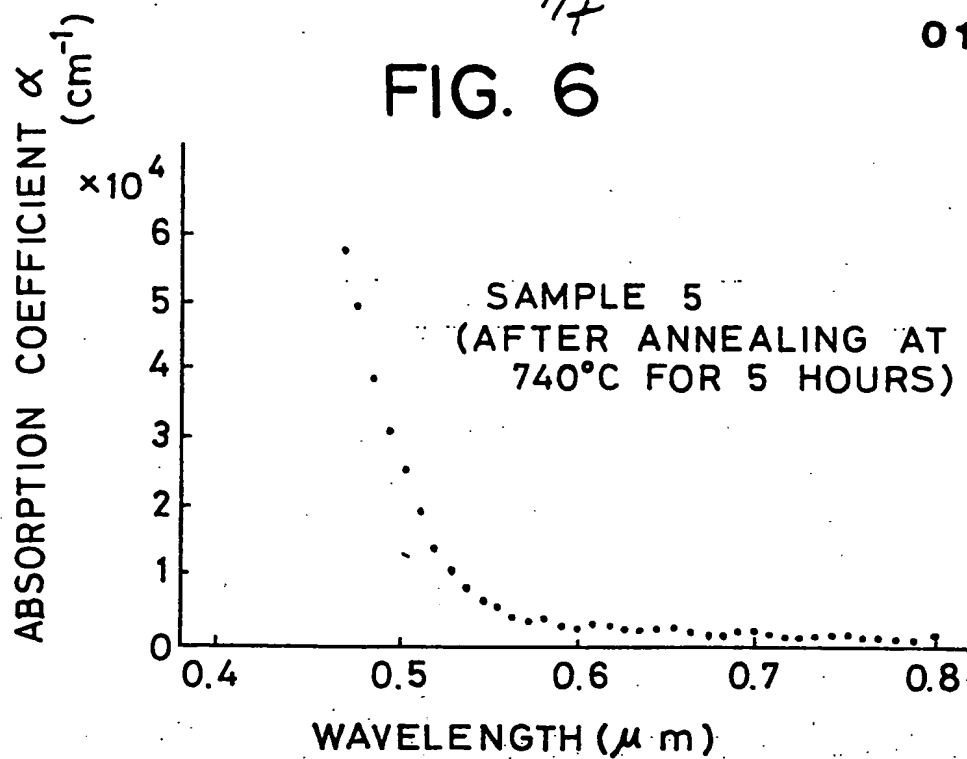
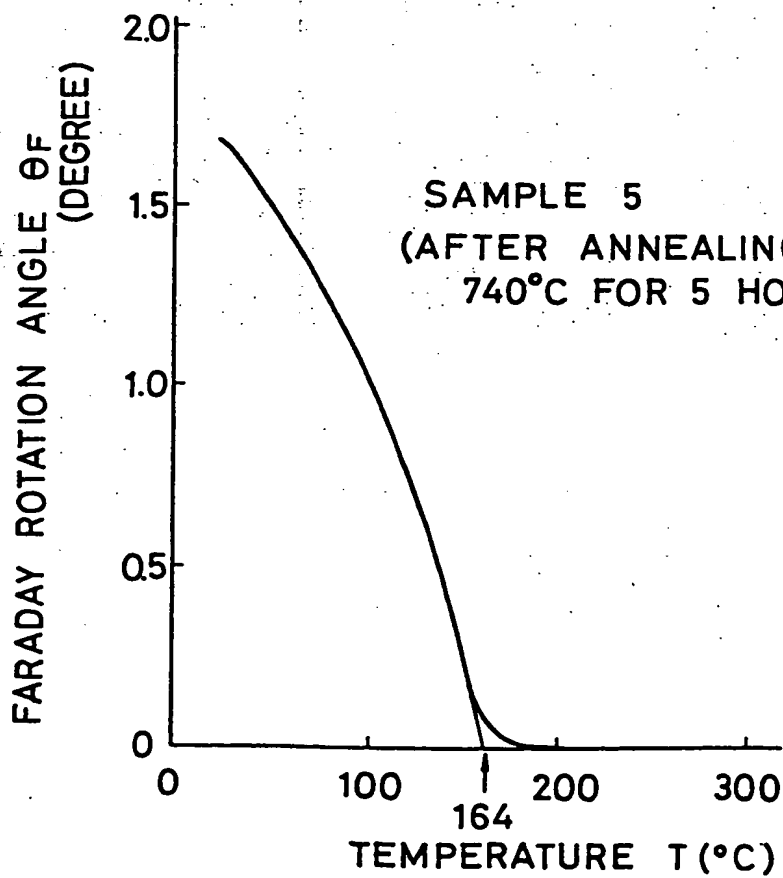
4/7
FIG. 6

FIG. 7



5/7

FIG. 8

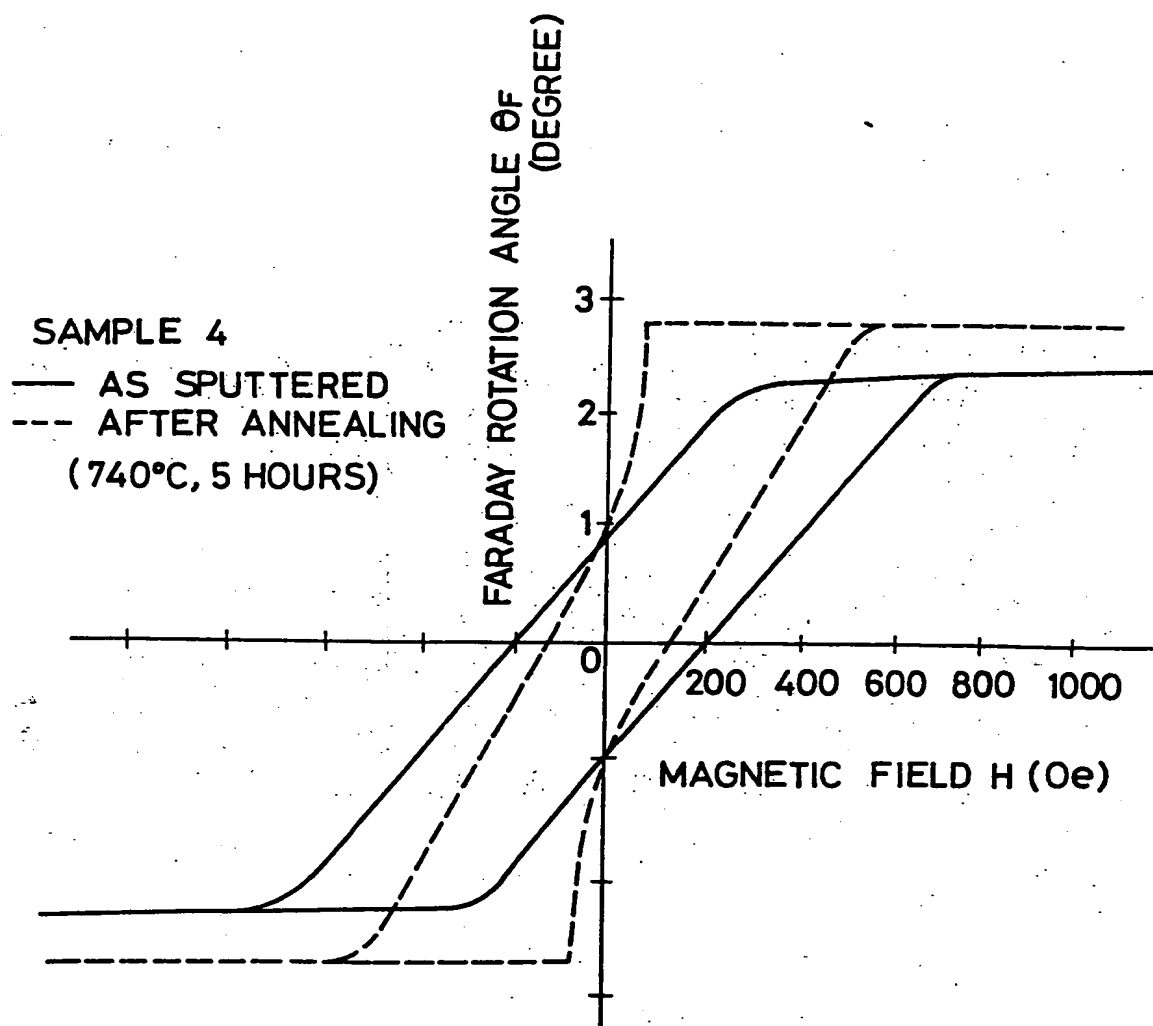


FIG. 9

SAMPLE 5
FILM THICKNESS
 $1.5 \mu\text{m}$

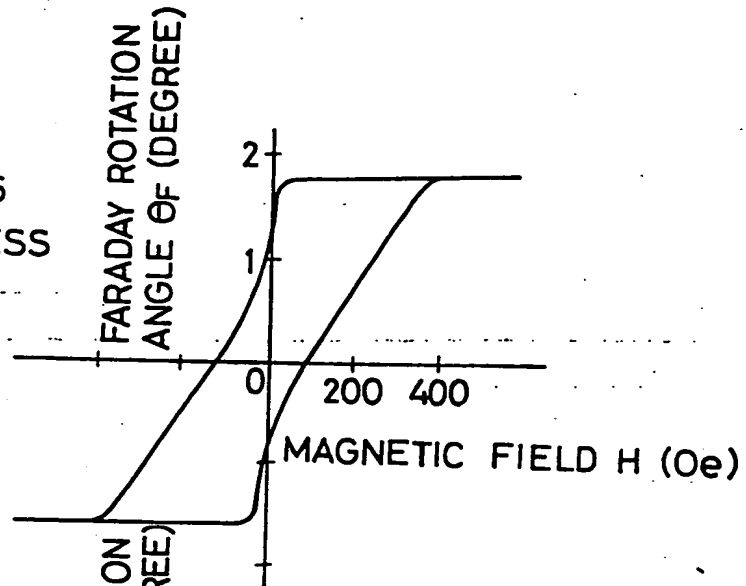


FIG. 10

SAMPLE 5
FILM THICKNESS
 $1.2 \mu\text{m}$

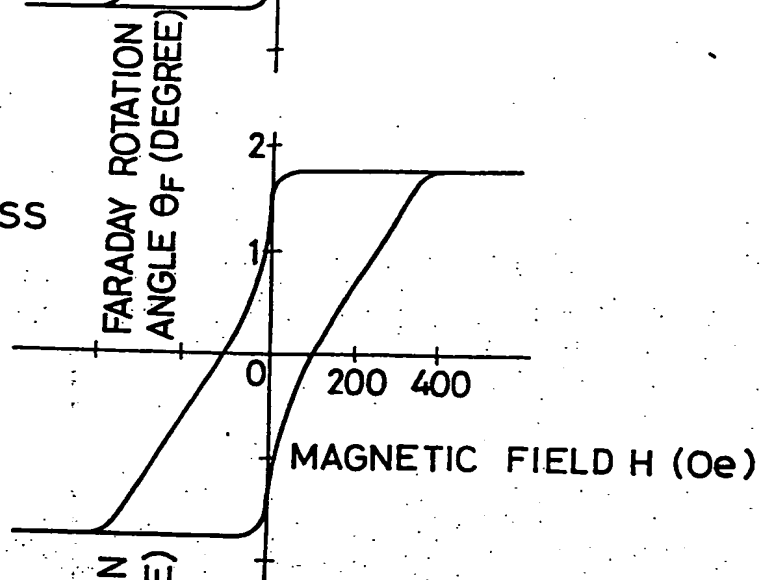


FIG. 11

SAMPLE 5
FILM THICKNESS
 $0.9 \mu\text{m}$

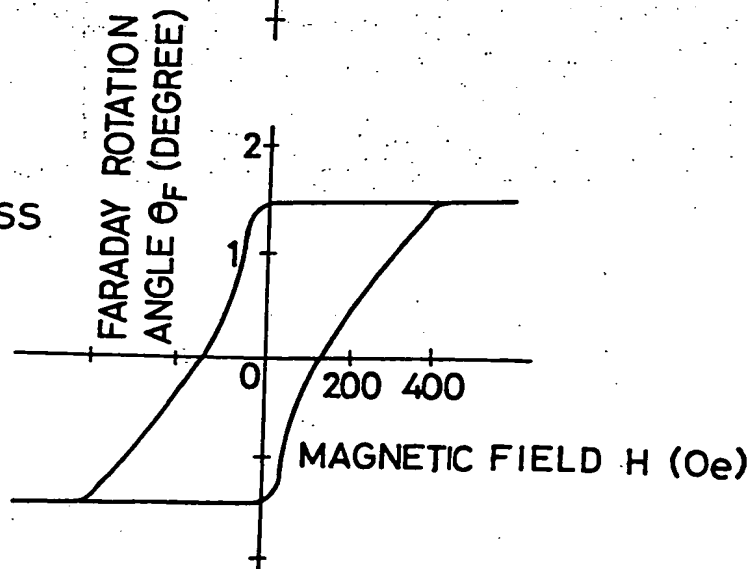


FIG. 12

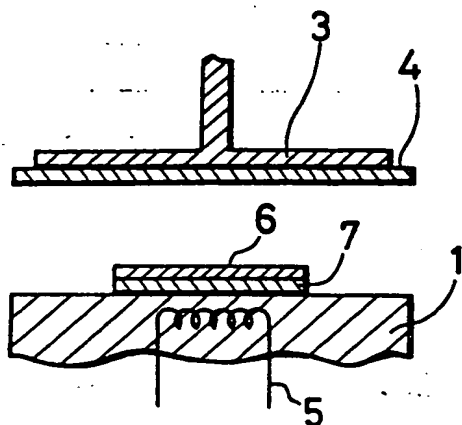


FIG. 14

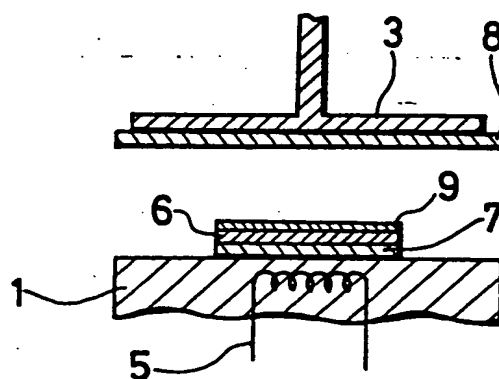
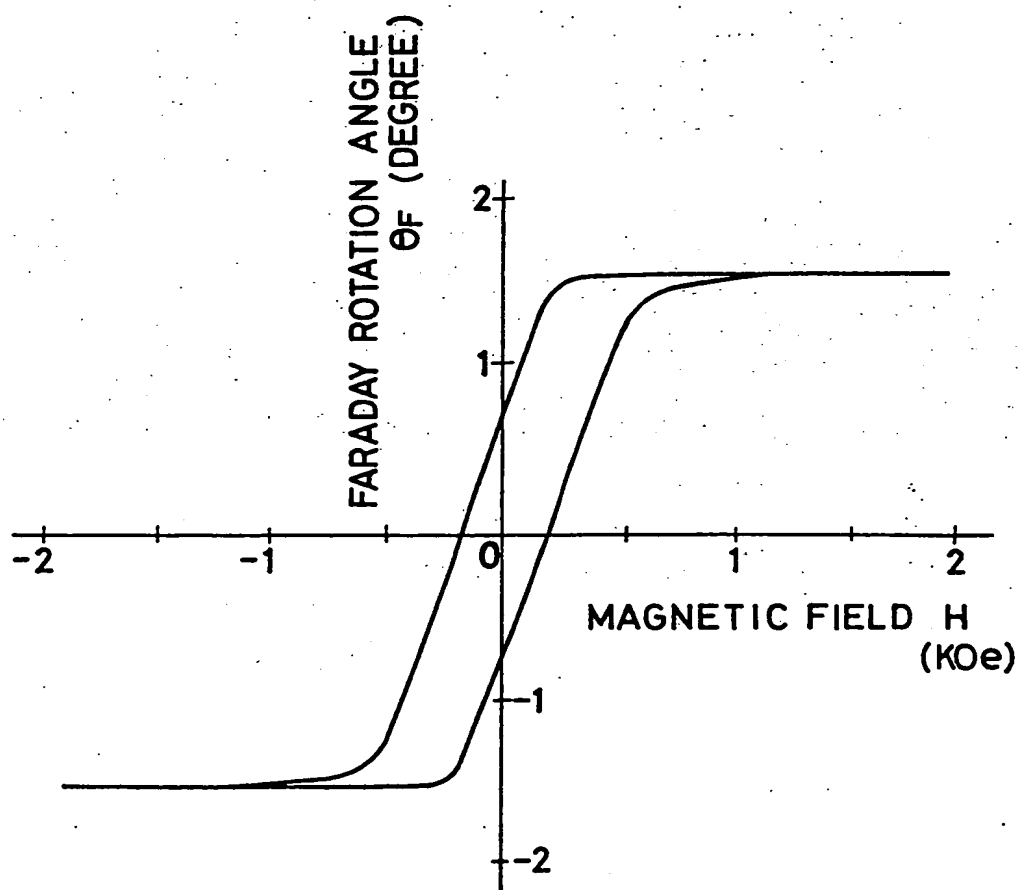


FIG. 13



INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP 84/00547

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int Cl ⁴ G11B11/10, H01F41/18		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC	G11B11/10, H01F41/18, H01F10/24	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴		
Jitsuyo Shinan Koho		1962 - 1984
Kokai Jitsuyo Shinan Koho		1971 - 1984
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ¹⁵	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	JP, A, 56-13710 (Nippon Electric Co., Ltd.) 10. February. 1981 (10.02.81) P.4, upper right column, lines 10 to 20 (Family nashi)	1, 6, 7
A	JP, A, 56-13710 (Nippon Electric Co., Ltd.) 10. February. 1981 (10.02.81) P.4, upper right column, lines 10 to 20 (Family nashi)	2-5
A	JP, A, 50-26096 (Hitachi, Ltd.) 18. March. 1975 (18.03.75) P.3, lower left column, line 16 to lower right column, line 4 (Family nashi)	1-7
A	JP, A, 50-20300 (Hitachi, Ltd.) 4. March, 1975 (04.03.75) P.3, lower left column, line 16 to lower right column, line 12 (Family nashi)	1-7
<p>¹ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹		Date of Mailing of this International Search Report ¹
February 1, 1985 (01.02.85)		February 18, 1985 (18.02.85)
International Searching Authority ¹		Signature of Authorized Officer ¹⁹
Japanese Patent Office		